

III.A.3 Composite Cathode for High Power Density Solid Oxide Fuel Cells

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Objectives

- Determine the electrochemical reaction kinetics of (La,Sr)(Co,Fe)O₃ (LSCF)-based cathode.
- Develop novel cathode structures.
- Determine the reactions between LSCF and zirconia. Develop a strategy to avoid reactions between LSCF and zirconia and promote electrochemical reactions.
- Determine the sensitivity of performance to sintering conditions.
- Demonstrate the feasibility of the LSCF composite cathode for use in high-performance solid oxide fuel cells (SOFCs) operating at low temperature.
- Determine the structural stability at operating temperature.

Approach

- Utilize idealized cathode structure to study the reaction pathway and rate-limiting steps for LSCF.
- Investigate LSCF-GDC (gadolinia-doped ceria) composite cathode structure that can help take advantage of the best properties of each material.
- Study the reaction of LSCF and zirconia and its effect on reaction kinetics.
- Determine the sensitivity of LSCF performance with respect to sintering conditions.
- Use GDC interfacial layer to prevent reaction, and study reaction kinetics at both idealized and practical interfaces.

Accomplishments

- Feasibility of LSCF-GDC cathode for high-performance SOFC has been well demonstrated. For low-temperature SOFC, a Ni-SDC (samarium-doped ceria) anode-supported cell with ceria electrolyte showed power density over 1 W/cm² at 623°C. Ni-YSZ anode-supported cell with yttria-doped zirconia (YSZ) electrolyte and a GDC interlayer showed 0.85 W/cm² and 1.6 W/cm² at 700°C and 800°C, respectively.
- For symmetric composite cathode samples, the LSCF-GDC cathode sample with GDC interlayer exhibited 0.3 Ω/cm² at 650°C, more than 50% lower resistance than a similarly fabricated LSCF-GDC sample without GDC interlayer.
- Basic kinetic data was obtained for LSCF using porous symmetric samples and the Adler-Lane-Steel (ALS) model.
- Screen printing processes have been developed for the interlayer and composite cathode for scale-up in the future.
- Initial attempts at accelerated testing have been made for symmetric cells as well as a Ni-YSZ anode-supported cell operating under elevated temperature.

Future Directions

- In order to determine long-term (40,000 hours) stability and compatibility with other SOFC components in a cost-effective way, a protocol for accelerated testing needs to be developed.
- Process scale-up for the anode-supported cell is needed.

Introduction

Reduction of SOFC operating temperature plays a key role in reducing stack cost by allowing the use of low-cost metallic interconnects and new approaches to sealing. Reported results for anode-supported SOFCs show that cathode polarization resistance is one of the primary barriers to achieving high power densities at operating temperatures $\leq 700^\circ\text{C}$. For example, one prior study of thin-electrolyte SOFCs showed that the low-current cathode interfacial resistance, R_i , was 70-85% of the total cell resistance from 550 - 800°C [1]. Thus, there is considerable current interest in new cathodes, other than the standard (La,Sr)MnO₃ (LSM)-YSZ compositions, for solid oxide fuel cells (SOFCs) that can operate at temperatures $\leq 700^\circ\text{C}$.

While the search for new cathode materials is valuable, there are known materials that show considerable promise for low-temperature applications. In particular, compositions containing (La,Sr)(Co,Fe)O₃ (LSCF) have been shown via impedance spectroscopy [2, 3, 4] to provide far superior performance compared to (La,Sr)MnO₃ (LSM) cathodes. For example, low-current polarization resistances measured for LSCF-GDC cathodes on YSZ electrolytes are $\approx 0.3 \Omega\text{cm}^2$ at 600°C and $\approx 0.03 \Omega\text{cm}^2$ at 700°C [3]. Despite these fundamental advantages, there has been little attempt to incorporate these cathodes into anode-supported SOFCs. This is due in part to the potential difficulties with this material. First, LSCF reacts readily with zirconia (at least for Co-containing compositions) to form resistive interfacial zirconate phases, severely limiting cathode performance [5]. Second, processing temperatures are low enough that progressive sintering during longer-term cell operation may compromise long-term stability.

Approach

This work includes a fundamental study of electrochemical reactions at controlled LSCF-YSZ

interfaces. Chemical reaction between LSCF and zirconia has been studied, and methods for mitigating the reactions, such as the inclusion of an interfacial ceria layer, have been investigated. A novel cathode composite structure has been developed, and demonstrations of their high performance under low temperature were done using Ni-based anode-supported cells. As a means to test the long-term stability of porous LSCF-based structures under SOFC operating conditions, initial attempts have been made at accelerated testing of symmetric cells as well as anode-supported cells under elevated temperature.

Results

The LSCF reaction kinetics has been studied using impedance arc from electrochemical impedance spectroscopy (EIS) characterization of symmetric half-cells. The half-cells of LSCF with thickness in the range of $30 \mu\text{m}$ were screen printed on both sides of bulk single-crystal YSZ electrolyte. The ALS model was used to fit the data, taking into account that for a mixed ionic conductor such as LSCF, the reaction zone is extended beyond three-phase boundaries. In this case, with an infinitely thick layer boundary condition, chemical resistance is expressed as follows:

$$R_{\text{chem}} = (RT/2F^2)[\tau/(1-\epsilon)aC_o^2D^*k]^{1/2} \quad [6]$$

Thick LSCF films should be appropriate for this model. Figure 1 shows a typical experimental impedance arc from LSCF/YSZ samples with fittings based on the ALS model. The fitting indicated a relatively good agreement with the ALS model, with estimated bulk diffusion coefficient and surface reactivity on the order of $D^* \sim 1 \times 10^{-8}$ and $k \sim 1 \times 10^{-5}$, respectively, which are on the same order of magnitude as those of similar materials such as LSC. However, the accuracy of the fitting was limited by high-frequency arc interfering on the left hand side of the arc. The source of high-frequency arc is unclear.

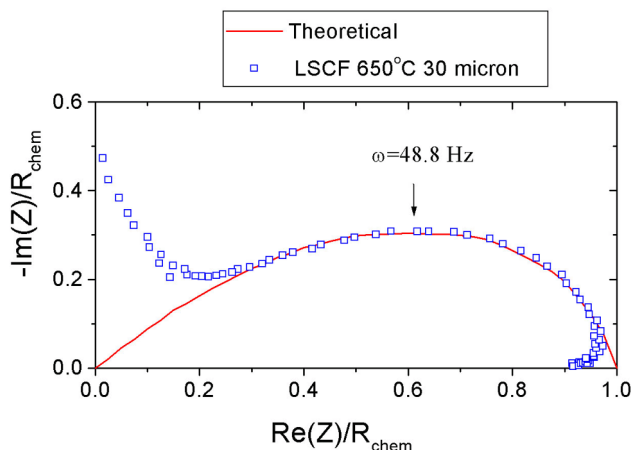


Figure 1. A Typical Experimental Arc from LSCF/YSZ Samples with Fittings Based on ALS Model

The dependence of the interfacial impedance of LSCF-GDC symmetric cathodes on sintering temperature was studied, with sintering temperatures varying from 900°C to 1100°C. The effect of sintering temperature is clear, with impedance decreasing as the sintering temperature increases, reaching minimum impedance of 0.6 Ω at 700°C and 0.17 Ω at 800°C for sintering temperature of 1025–1050°C. While this value is an order of magnitude higher than that achieved in previous work [3], it is likely that the value is limited by LSCF-YSZ reaction as well as the microstructure not being optimized for active reaction surface area. Further increases in sintering temperature increased the impedance, reaching $\sim 3.5 \Omega\text{cm}^2$ at 1100°C. This is likely due to sintering of pore structure as well as further reaction between LSCF-YSZ.

Figure 2 compares the polarization resistance of LSCF-GDC cathode with and without GDC interlayer vs. inverse temperature from the symmetric half-cell samples. The resistances correspond to 0.3 Ωcm^2 and 0.7 Ωcm^2 at 650°C with and without GDC, respectively, for the single interface case of typical cells. The slope of the graph with inverse T for both of the samples are almost identical, indicating that the GDC interlayer does not have significant effect on the rate-limiting step.

Figure 3 shows the button cell performance at various temperatures for the Ni-YSZ anode-supported cell with YSZ electrolyte / GDC interlayer

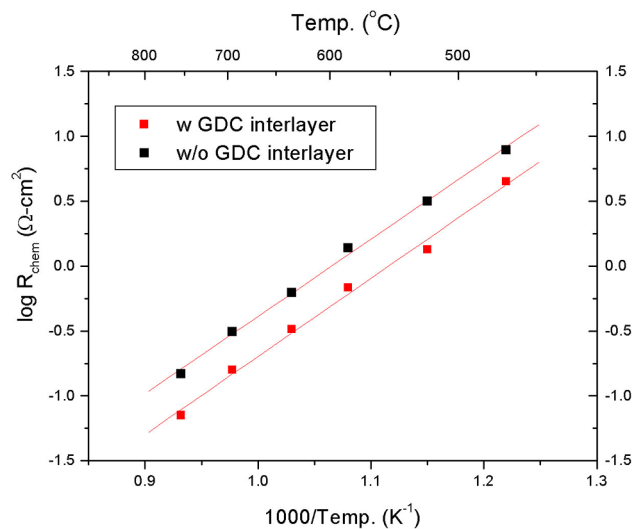


Figure 2. Polarization Resistances of LSCF-GDC Cathode with and without GDC Interlayer vs. Inverse Temperature

/ LSCF-GDC cathode. The thicknesses of YSZ electrolyte and GDC interlayers are 8 μm and 3 μm , respectively. Both the GDC layer and LSCF-GDC cathode were screen printed. As shown in Figure 3 (top), open circuit potentials (OCPs) are close to theoretical values corresponding to air on the cathode side and 3% $\text{H}_2\text{O}-\text{H}_2$ fuel on the anode side. The maximum power densities at 800°C and 700°C are about 1.6 W/cm^2 and 0.8 W/cm^2 , respectively (Figure 3, bottom). AC impedance analysis results showed that at 800°C, the ohmic resistance is about 0.13 Ωcm^2 , while the total electrode resistance including the anode and cathode is about 0.17 Ωcm^2 . At 700°C, they are 0.215 Ωcm^2 and 0.26 Ωcm^2 , respectively. In order to evaluate the performance of the cathode under lower temperature, Ni-SDC anode-supported cells were used with SDC electrolyte and LSCF-GDC cathode. An excellent power density of $\sim 1 \text{ W}/\text{cm}^2$ was obtained at 623°C, indicating substantially better performance compared to the Ni-YSZ supported cell with YSZ electrolyte shown above. This and subsequent EIS tests on the Ni-SDC cells indicated that the cathode performance is not a limiting factor on the performance of the cells under operation temperature as low as 600°C. In fact, the open circuit voltage at 623°C was only $\sim 0.9 \text{ V}$, suggesting that even better performance is probable with LSCF-GDC cathode, if it were not due to the electronic conductivity of SDC.

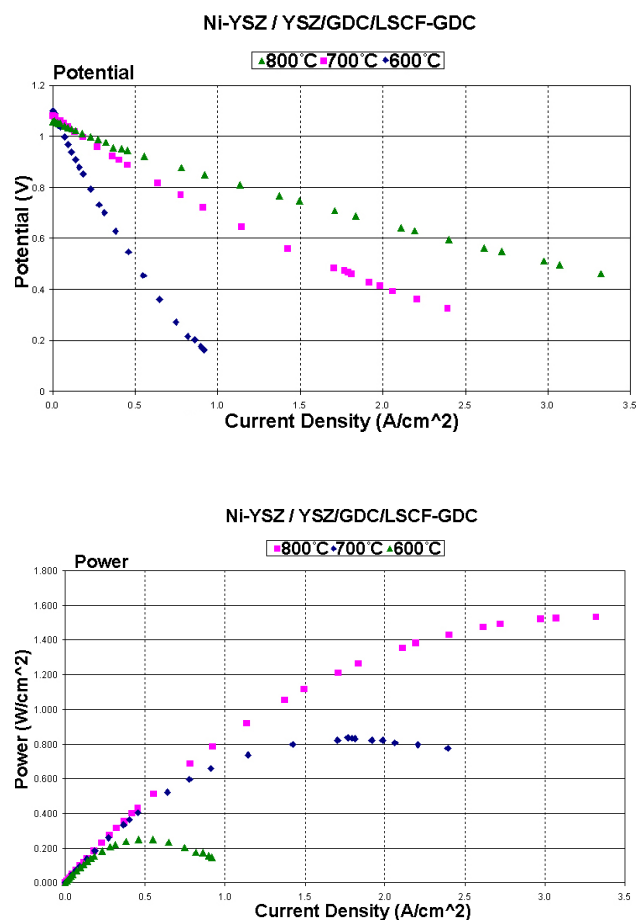


Figure 3. (top) Performance of Ni-YSZ Anode-Supported Cell with YSZ Electrolyte / GDC Interlayer / LSCF-GDC - Potential
(bottom) Power Density Plot of the Same Cell

Conclusions

The feasibility of LSCF-GDC composite cathode for low-temperature, high-performance SOFCs has been amply demonstrated. For further development, long-term stability and compatibility of the LSCF need to be verified, preferably via appropriate accelerated testing.

References

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